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~~Preparation of alkapolyenyl compounds, use of particular
cocatalysts and use of the process products~~

- 5 The present invention relates to a process for preparing
alkapolyenyl compounds by homogeneously catalyzed reaction of
1-substituted alka-2,7-dienes and/or 3-substituted
alka-1,7-dienes with 1,3-conjugated dienes in the presence of
rhodium compounds, to the use of mineral acids and organic
10 halides as cocatalysts in this reaction and to the use of the
process products in the preparation of surface-active materials.

- Long-chain alcohols are a basic constituent of numerous
surfactants. Suitable alcohols can be obtained industrially in
15 many ways, for example via hydroformylation of long-chain
olefins, Ziegler alcohol syntheses or by extracting them from
natural sources. A particularly inexpensive route is the
preparation of surfactant alcohols based on butadiene or
derivatives thereof as building blocks. For example, branched or
20 linear dodecanols can be obtained by appropriate reaction of
dodecatrienyl ethers or esters.

- Syntheses of suitable polyenyl compounds are known. Thus, for
example, GB-A-1316725 describes the rhodium-catalyzed
25 codimerization of 1-substituted 2,7-octadienes, e.g.
1-acetoxy-2,7-octadiene, 1-methoxy-2,7-octadiene and
1-phenoxy-2,7-octadiene, with 1,3-conjugated dienes, e.g.
1,3-butadiene and isoprene, in solvents such as ethanol, acetic
acid, acetone, benzene, methylene chloride, tetrahydrofuran,
30 acetonitrile, dimethylformamide or dimethylacetamide using
various rhodium compounds such as rhodium trichloride, rhodium
tribromide, rhodium trinitrate, dirhodium tetraacetate,
tetrakis(ethylene)dichlorodirhodium and
bis(cycloocta-1,5-diene)dichlorodirhodium with addition of
35 various polymerization inhibitors, e.g. t-butylcatechol,
phenothiazine, tetrabutoxytitanium and titanium tetrachloride,
and also phosphorus-containing compounds, e.g.
tri-n-butylphosphine, tricyclohexylphosphine, triphenylphosphine
and triphenoxyphosphine.

- 40 Processes developed on the basis of these catalyst systems are
described and make suggestions for increasing the catalyst
activity.

According to the Japanese patent publication No. 77-38533, the catalytic activity can be increased, for example, by carrying out the reaction in the presence of hydrogen.

- 5 GB-A-2107700 proposes adding chromium halides to the reaction mixture. The rhodium-catalyzed codimerization of 1-acetoxy-2,7-octadiene or 1-phenoxy-2,7-octadiene with 1,3-butadiene with addition of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is described. Apart from rhodium trichloride, use is made of
- 10 bis(π -crotyl)tetrachloro(butadiene)dirhodium.

In GB-A-2107701, the addition of chromium compounds and also of organic halides such as crotyl chloride or cinnamyl chloride is described as being advantageous for the reaction of

- 15 1-hydroxyalkoxy-2,7-octadienes or derivatives thereof, e.g.
1-(2'-hydroxyethoxy)-2,7-octadiene,
1-(2'-acetoxyethoxy)-2,7-octadiene,
1-(2'-methoxyethoxy)-2,7-octadiene,
1-(3'-hydroxypropoxy)-2,7-octadiene or
- 20 1-(4'-hydroxybutoxy)-2,7-octadiene, with 1,3-butadiene. An analogous statement is made in GB-A-2108104 in respect of the reaction of 1-acyloxy-2,7-octadienes, e.g.
1-acetoxy-2,7-octadiene, 1-propionyloxy-2,7-octadiene or 1-pivaloxy-2,7-octadiene, with 1,3-butadiene.

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The above statements are largely confirmed by Bochmann et al. in Journal of Molecular Catalysis, 22 (1984) 363-365 and in Journal of Molecular Catalysis, 26 (1984) 79-88. It is reported that organic chlorides containing activated C-Cl bonds, in particular

- 30 allyl chlorides, and also hydrated chromium(III) chloride accelerate the reaction of 1-acetoxy-2,7-octadiene with 1,3-butadiene. On the other hand, phosphines, amines, molecular nitrogen, water, ethanol and also ionic chlorides, for example $\text{NMe}_4^+\text{Cl}^-$, are said to slow the reaction, which is why the effect
- 35 of hydrated chromium trichloride is not understood. Moreover, the use of the chromium compound leads to a heterogeneous system in which the chromium compound forms the solid phase and the catalyst is dissolved in the liquid phase. This is critical in terms of process engineering.

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However, the organic halides which are advantageous in this respect because they are generally soluble in the reaction medium often do not effect a sufficient increase in activity. This is, in particular, the case when alkapolyyenyl ethers are to be

- 45 reacted, i.e., for example, with a view to the economically

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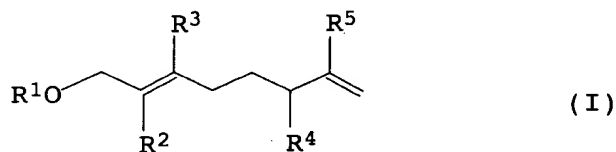
important synthesis of dodecatrienyl ethers such as methoxydodecatrienyl compounds.

The object of providing an advantageous process for preparing alkapolienyl compounds by homogeneously catalyzed reaction of substituted alkadienes with 1,3-conjugated dienes in the presence of rhodium compounds is surprisingly achieved according to the present invention by the use of mineral acids and inorganic halides which can be dissolved in the reaction mixture.

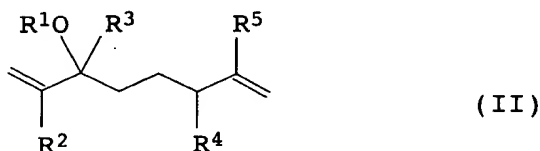
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The present invention accordingly provides a process for preparing alkapolienyl compounds by homogeneously catalyzed reaction of 1-substituted alka-2,7-dienes of the formula I and/or 3-substituted alka-1,7-dienes of the formula II,

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where

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R¹ is hydrogen or C₁-C₆-alkyl, C₅-C₈-cycloalkyl, C₁-C₆-alkanoyl, C₆-C₁₂-aryl, C₆-C₁₂-aryloyl or C₇-C₁₈-aralkyl which may each be unsubstituted or monosubstituted, disubstituted or trisubstituted by hydroxy, C₁-C₆-alkoxy, C₁-C₆-alkanoyloxy and/or halogen, and

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R², R³, R⁴ and R⁵ are, independently of one another, hydrogen or C₁-C₆-alkyl,

with 1,3-conjugated dienes of the formula III,

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where

R^6 and R^7 are, independently of one another, hydrogen or C_1-C_6 -alkyl, and

5 R^8 is hydrogen, C_1-C_6 -alkyl or C_2-C_6 -alkenyl,

in the presence of rhodium compounds, wherein at least one mineral acid and/or at least one inorganic halide is dissolved in the reaction mixture.

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For the purposes of the present invention, a homogeneously catalyzed reaction is one in which the catalytic constituents, i.e. catalysts and cocatalysts, do not form a heterogeneous phase, i.e. do not form, in particular, a solid phase under the

15 reaction conditions. They are generally present in the phase in which the reaction of the reactants of a reaction mixture takes place. The reaction mixture itself can consist of one or more phases. If the reaction mixture consists of a plurality of phases, the catalytic constituents and/or the reactants can also
20 be distributed over two, three or possibly more phases. In such a case, the reaction can take place in only one phase, in two phases or possibly also in more than two phases.

In one embodiment of the present invention, the reaction mixture
25 consists of a single phase and this phase is liquid. In a particular embodiment, the reaction mixture consists of a plurality of phases and the phases are liquid and/or gaseous. In a two-phase mixture, it is usual for one phase to be liquid and the other to be gaseous. In a three-phase mixture, it is
30 generally the case that two phases are liquid and one is gaseous, for example liquid/liquid mixtures such as reaction mixtures of organic liquid and aqueous liquid together with a gaseous phase comprising gaseous reactants, for example dienes of the formula (III) which are gaseous under the reaction conditions, e.g.
35 butadiene, and/or cocatalysts. Part of the constituents present in the gaseous phase is generally also present in solution in the liquid phase or phases.

Mineral acids which are suitable for use in the process of the
40 present invention include, for example, hydrogen chloride, sulfuric acid, nitric acid, phosphoric acid, HBF_4 , HPF_6 and $HSbF_6$. Preference is given to hydrogen chloride. Mineral acids can be dissolved in the reaction mixture by mixing the mineral acids as such or mineral acid solutions with the other constituents of the
45 reaction mixture. If mineral acid solutions are used, preference

is given to aqueous solutions, i.e. particularly hydrochloric acid.

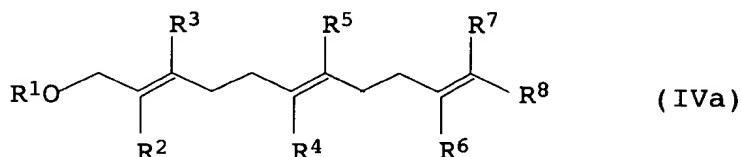
- Suitable inorganic halides include, for example, alkali metal, 5 alkaline earth metal and transition metal chlorides and bromides and also chlorides and bromides of elements of main groups III, IV, V and VI. Halides which have been found to be advantageous are those halides which are sensitive to hydrolysis, i.e. they react with water to form the corresponding hydrohalic acids. In 10 this way, hydrohalic acids can be formed in situ. Chlorides are generally preferred. Examples of suitable halides are $ZrCl_4$, $SnCl_4$, $TiCl_4$ and especially $GeCl_4$ and WCl_6 . The inorganic halides are generally solid or liquid. If they are solid, suitable halides such as WCl_6 dissolve in sufficient amounts in the 15 reaction mixture. The halides can be combined with the other constituents of the reaction mixture either as such or in dissolved form. If solutions are used, preference is given to aqueous solutions.
- 20 Suitable amounts of dissolved mineral acid and/or dissolved inorganic halide are in the range from 1 to 10^5 mol, preferably from 5 to 10^3 mol, per gram atom of rhodium. It is usual to use a deficiency of dissolved mineral acid and/or dissolved inorganic halide, based on the amount of alkadiene to be reacted, 25 preferably a molar ratio of from 0.5 to 10^{-3} . Accordingly, the cocatalysts used according to the present invention should have a solubility of at least about 10 mg/l in the reaction mixture. Preference is given to solubilities of at least 50 mg/l and in particular at least 100 mg/l.
- 30 In a particular embodiment of the present invention, the reaction is carried out in the presence of further compounds which are known to have a favorable effect on the type of reaction carried out according to the present invention, in particular on reaction 35 rate and selectivity. An example which may be mentioned in this context is hydrogen gas which is generally added under moderate pressure, preferably from 5 to 20 bar. The addition of organic halides can also be advantageous. In this context, attention is drawn to the organic halides described in GB-A-2107701 and 40 GB-A-2108104. Organic halides which are particularly suitable for the purposes of the present invention are benzotrichloride, allyl chloride, crotyl chloride, benzylidene chloride and cinnamyl chloride. The amount of dissolved organic halide is generally in the order of magnitude which is chosen according to the present 45 invention for the amounts of dissolved mineral acid and/or inorganic halides.

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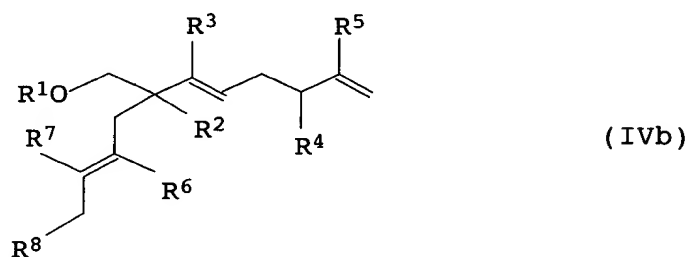
The reaction of 1-substituted alka-2,7-dienes of the formula I with 1,3-conjugated dienes of the formula III generally leads to a mixture of linear and branched alkapolyenyl compounds, in particular the compounds of the formulae IVa, IVb and IVc:

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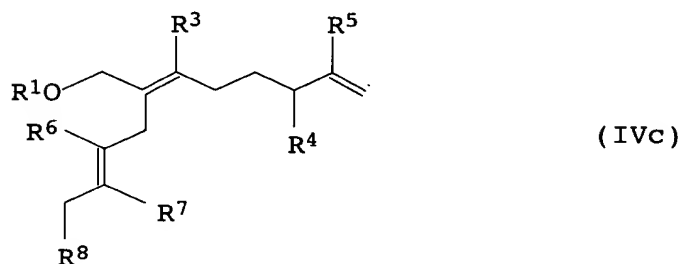


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where R^1 to R^8 are as defined above and isomerization of the double bonds can occur during the course of the reaction being catalyzed according to the present invention.

35 The ratio of compounds of the formula IVa to compounds of the formulae IVb and/or IVc is referred to as the n/iso ratio. The mixtures obtainable by the process of the present invention generally have an n/iso ratio of from 0.2 to 2.5.

40 The reaction of 3-substituted alka-1,7-dienes of the formula II with 1,3-conjugated dienes of the formula III generally also leads to a complex mixture of linear and branched alkapolyenyl compounds.

45 The expression C_1 - C_6 -alkyl refers to linear or branched hydrocarbon radicals having 1 to 6 carbon atoms, for example methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl, i-butyl,

t-butyl, n-pentyl, i-pentyl, neopentyl and n-hexyl. Preference is given to C₁-C₄-alkyl groups, in particular methyl and ethyl.

The expression C₁-C₆-alkoxy refers to C₁-C₆-alkyl-O-, where
 5 C₁-C₆-alkyl is as defined above.

The expression alkanoyl refers to C₁-C₆-alkyl-C(O)-, where
 C₁-C₆-alkyl is as defined above.

10 The expression alkanoyloxy refers to C₁-C₆-alkyl-C(O)O-, where
 C₁-C₆-alkyl is as defined above.

The expression halogen refers, for example, to fluorine, chlorine, bromine or iodine, preferably fluorine or chlorine.

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The expression C₃-C₈-cycloalkyl refers to cyclic hydrocarbon radicals having 3 to 8 carbon atoms, for example cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl.

20 The expression C₆-C₁₂-aryl refers to aromatic radicals having from 6 to 12 carbon atoms, for example phenyl, naphthyl and biphenyl. Preference is given to phenyl.

The expression C₆-C₁₂-aryloyl refers to C₆-C₁₂-aryl-C(O)-, where

25 C₆-C₁₂-aryl is as defined above.

C₇-C₁₈-Aralkyl refers to C₆-C₁₂-aryl-C₁-C₆-alkylene, where C₆-C₁₂-aryl is as defined above and C₁-C₆-alkylene is derived from the abovementioned C₁-C₆-alkyl groups and is, for example,

30 methylene, 1,1- or 1,2-ethylene, 1,1-, 1,2-, 1,3- or 2,2-propylene. Preference is given to benzyl.

Examples of hydroxy-substituted C₁-C₆-alkyl groups are hydroxymethyl, 2-hydroxyeth-1-yl, 3-hydroxyprop-1-yl,

35 4-hydroxybut-1-yl. Preference is given to 2-hydroxyeth-1-yl.

Examples of C₁-C₆-alkoxy-substituted C₁-C₆-alkyl groups are methoxymethyl, 2-methoxyeth-1-yl, 3-methoxyprop-1-yl, 4-methoxybut-1-yl.

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Examples of C₁-C₆-alkanoyloxy-substituted C₁-C₆-alkyl groups are acetoxymethyl, 2-acetoxyeth-1-yl, 3-acetoxyprop-1-yl, 4-acetoxybut-1-yl.

45 Examples of halogen-substituted C₁-C₆-alkyl groups are trifluoromethyl and trichloromethyl.

The expression C₂-C₆-alkenyl refers to monounsaturated hydrocarbon radicals having from 2 to 6 carbon atoms which are derived from the above-defined C₂-C₆-alkyl radicals, for example prop-2-en-1-yl and but-3-en-1-yl.

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In a particular embodiment of the present invention, the reaction is carried out using alkadienyl ethers, i.e., for example, the 1-substituted alka-2,7-dienes of the formula I and/or the 3-substituted alka-1,7-dienes of the formula II in which R¹ is
 10 C₁-C₆-alkyl, in particular methyl or ethyl, C₃-C₈-cycloalkyl, C₆-C₁₂-aryl, in particular phenyl, or C₇-C₁₈-aralkyl, in particular benzyl, each of which may be unsubstituted or monosubstituted, disubstituted or trisubstituted by hydroxy, C₁-C₆-alkoxy, C₁-C₆-alkanoyloxy, in particular acetoxy, and/or halogen.

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In a particularly preferred embodiment, the reaction is carried out using 1-alkoxyalka-2,7-dienes, in particular 1-methoxyalka-2,7-dienes and/or 3-alkoxyalka-1,7-dienes, in particular 3-methoxyalka-1,7-dienes.

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As an alternative, 1-hydroxyalkoxyalka-2,7-dienes, in particular 1-(2'-hydroxyethoxy)alka-2,7-dienes and/or 3-hydroxyalkoxyalka-1,7-dienes, in particular 3-(2'-hydroxyethoxy)alka-1,7-dienes, can be reacted.

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In a further particular embodiment, the reaction is carried out using 1-substituted octa-2,7-dienes and/or 3-substituted octa-1,7-dienes, i.e. compounds of the formula I or II in which R² to R⁵ are hydrogen.

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In a particular, preferred embodiment, 1-methoxyocta-2,7-diene and/or 3-methoxyocta-1,7-diene are reacted.

As an alternative, 1-(2'-hydroxyethoxy)octa-2,7-diene and/or

35 3-(2'-hydroxyethoxy)octa-1,7-diene can be reacted.

The above-described starting materials can be prepared in a known manner (A. Behr in "Aspects of Homogeneous Catalysis", Vol. 5, pp. 3-73, 1984 and also the literature cited therein). In

40 principle, 1,3-conjugated dienes, for example those of the formula III, are reacted with appropriate carboxylic acids or alcohols. If carboxylic acids are used, this gives alka-2,7-dien-1-olate esters and/or alka-1,7-dien-3-olate esters. If alcohols are used, then alka-2,7-dien-1-olate ethers and/or
 45 alka-1,7-dien-3-olate ethers are obtained. Thus, it is possible either to react carboxylic acids such as acetic acid, propionic acid, butyric acid or benzoic acid with 1,3-butadiene to form

1-acyloxyocta-2,7-dienes and/or 3-acyloxyocta-1,7-dienes, or to react alcohols, for example alkanols such as methanol, ethanol or ethylene glycol, phenol or benzyl alcohol with 1,3-butadiene to give the corresponding 1-alkoxyocta-2,7-dienes and/or

5 3-alkoxyocta-1,7-dienes, 1-hydroxyalkoxyocta-2,7-dienes and/or 3-hydroxyalkoxyocta-1,7-dienes, 1-aryloxyocta-2,7-dienes and/or 3-aryloxyocta-1,7-dienes or 1-aralkoxyocta-2,7-dienes and/or 3-aralkoxyocta-1,7-dienes. Catalysts suitable for this type of reaction are, for example, catalysts based on palladium, for

10 example palladium acetate, and phosphorus compounds such as triarylphosphines or triaryl phosphites, for example triphenylphosphine or tris(o-tolyl) phosphite.

In a particular embodiment of the present invention, the reaction

15 is carried out using 1,3-conjugated dienes of the formula III in which R^6 and R^7 are, independently of one another, hydrogen or C_1 - C_6 -alkyl and R^8 is hydrogen. If R^6 and/or R^7 are C_1 - C_6 -alkyl, then preference is given to methyl.

20 In a particularly preferred embodiment, R^6 and R^7 are hydrogen and R^8 is hydrogen, C_1 - C_6 -alkyl, in particular methyl, or C_2 - C_8 -alkenyl, in particular but-3-en-1-yl.

Very particular preference is given to the reaction of the

25 1,3-conjugated dienes isoprene, 2,3-dimethylbutadiene, piperylene, octa-1,3,7-triene, 2,6-dimethylocta-1,3,7-triene, 2,7-dimethylocta-1,3,7-triene and in particular 1,3-butadiene.

The 1,3-conjugated dienes to be reacted according to the present

30 invention can be prepared in a manner known per se or can be procured commercially.

The molar ratio of alkadienes to 1,3-conjugated dienes used in the reaction of the present invention is generally in a range

35 from about 1:10 to 10:1, preferably from 2:1 to 1:5 and in particular from 1:1 to 1:3. The alkadiene component can be an essentially pure compound or it can be a mixture of two or more compounds, in particular a mixture of 1-substituted alka-2,7-dienes and 3-substituted alka-2,7-dienes. Such mixtures

40 are frequently obtained as process products in the preparation of these compounds. If mixtures are used, preference is given to those which are rich in 1-substituted alka-1,7-dienes. Mixtures containing at least 80% and in particular at least 95% of 1-substituted alka-2,7-dienes are advantageous. The

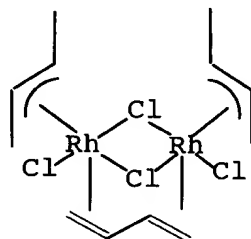
45 1,3-conjugated dienes can also be mixtures of two or more compounds, but preference is given to the essentially pure

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compounds as are offered, for example, for synthetic purposes, i.e. having a purity of at least 99%.

Suitable rhodium compounds include, for example, inorganic or
 5 organic rhodium salts and organic rhodium complexes. The inorganic salts are generally rhodium(III) salts containing customary anions, for example, chloride, bromide or nitrate. The organic salts are generally rhodium(III) salts containing customary carboxylate anions, for example acetate, or
 10 acetylacetonates. Suitable complexes are, in particular, π -allyl complexes in which the rhodium is likewise formally present in the oxidation state III, for example tetrakis(π -allyl)dichlorodirrhodium, tetrakis(ethylene)dichlorodirrhodium and
 15 bis(cycloocta-1,5-diene)dichlorodirrhodium. Particular preference is given to bis(π -crotyl)tetrachloro(butadiene)dirrhodium of the formula

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The reaction of the present invention can be carried out in the presence of one or more rhodium compounds. Rhodium compounds are preferably used in amounts ranging from 10^{-6} to 10^{-1} gram atom,
 30 preferably from 10^{-5} to 10^{-3} gram atom and in particular from 2×10^{-5} to 5×10^{-4} gram atom, of rhodium per mole of alkadiene.

The process of the present invention is generally carried out in a suitable reactor, for example an autoclave, at from 0°C to
 35 250°C , preferably from 60°C to 130°C . With a view to the catalyst stability, it can be advantageous to work at relatively low temperatures, for example in the region of 60°C . The reaction can also be carried out under superatmospheric pressure, for example in a range from 5 to 20 bar, particularly when a gaseous
 40 component such as hydrogen is added to the reaction mixture.

Further embodiments can be derived by appropriate combination of the above-described particular and/or preferred embodiments.

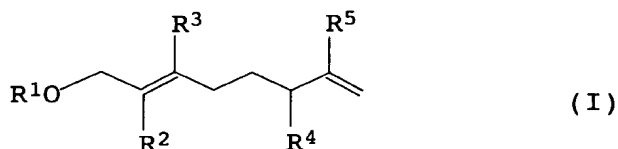
45 The present invention further provides for the use of a mixture of alkapolyenyl compounds obtainable by the process of the present invention in the preparation of surface-active materials

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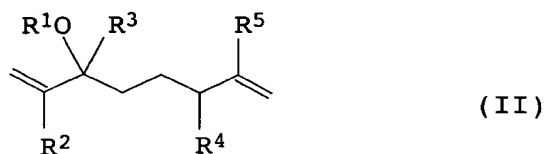
such as surfactants and detergents. The process products obtained according to the present invention serve, in particular, as intermediates in the preparation of long-chain fatty alcohols having from 12 to 20 carbon atoms. In particular, the process products are suitable for preparing branched and/or linear dodecanols, for example lauryl alcohol. For use as intermediates, the process products can be employed in the form in which they are obtainable by the process of the present invention or they can be worked up first, for example by increasing the n/iso ratio. Any water and/or low-boiling by-products, e.g. octatriene, present can be removed, for example, by distillation of the process product. If desired, the catalyst together with the remaining bottoms can be returned to the reaction.

The present invention further provides for the use of at least one mineral acid and/or at least one inorganic halide as cocatalyst dissolved in the reaction mixture of the homogeneously catalyzed reaction, carried out in the presence of rhodium compounds, of 1-substituted alka-2,7-dienes of the formula I and/or 3-substituted alka-1,7-dienes of the formula II,

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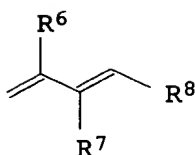


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where R¹ is hydrogen or C₁-C₆-alkyl, C₅-C₈-cycloalkyl, C₁-C₆-alkanoyl, C₆-C₁₂-aryl, C₆-C₁₂-aryloyl or C₇-C₁₈-aralkyl each of which may be unsubstituted or monosubstituted, disubstituted or trisubstituted by hydroxy, C₁-C₆-alkoxy, C₁-C₆-alkanoyloxy and/or halogen, and R², R³, R⁴ and R⁵ are, independently of one another, hydrogen or C₁-C₆-alkyl, with 1,3-conjugated dienes of the formula III

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(III)

where R^6 and R^7 are, independently of one another, hydrogen or $\text{C}_1\text{-C}_6\text{-alkyl}$, and R^8 is hydrogen, $\text{C}_1\text{-C}_6\text{-alkyl}$ or $\text{C}_2\text{-C}_6\text{-alkenyl}$.

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In the present case, a cocatalyst is a compound which favorably influences the catalytic activity of rhodium catalysts in the above-described homogeneously catalyzed reaction, for example increase the reaction rate and/or the selectivity. Preferred
15 embodiments of this use according to the present invention may be derived from the above-described embodiments of the process of the present invention.

The following examples illustrate the invention without
20 restricting its scope.

Examples

A baked-out glass autoclave (Comparative Ex. and Ex. 1, 2, 5:
25 50 ml; Ex. 3, 4, 6-8: 250 ml) was charged with bis(π -crotyl)tetrachloro(butadiene)dirhodium (Rh complex), 1-methoxy-2,7-octadiene (MOOD) and, if appropriate, mineral acid, inorganic halide and/or organic halide (Ex. 4: 0.50 g of benzotrichloride). Butadiene was condensed in at 0°C . The mixture
30 was heated at 120°C for 2 hours. The reaction mixture was then cooled and analyzed by gas chromatography (column: OV-1-DF-0.25 (50 m x 0.32 mm) using an FID. As internal standard, use was made of dodecane, either as an addition to the reaction mixture (Comparative Ex. and Ex. 1, 2, 5: about 0.80 g) or by addition in
35 the gas-chromatographic analysis. The amounts of starting materials used, the conversion of 1-methoxyocta-2,7-diene, the reaction rate expressed as the number of 1-methoxy-octa-2,7-diene molecules reacted in 1 hour per rhodium atom and the selectivity based on methoxydodecatrienyl compounds are shown in Table 1
40 below.

Table 1:

Example	Rh complex [mg]	MOOD [g]	Butadiene [g]	Addition		Con- version [%]	Reaction rate [mol/mol·h]	Selectivity [%]
				Type	[g]			
Comparative	6.5	3.50	3.2	-	-	35.5	174	97.0
1	6.5	3.50	4.0	GeCl ₄	1.10	83.9	411	87.0
2	6.8	3.50	3.2	WCl ₆	0.20	56.1	263	93.0
3	6.5	35	40.6	GeCl ₄	1.05	52.1	2554	100.0
4	3.25	35	42.5	GeCl ₄	0.50	33.4	3227	99.7
5	6.6	3.50	3.2	HCl; aq. 10 %	0.05	91.6	442	62.0
6	6.6	35	28.7	HCl; aq. 32 %	0.58	62.9	3039	97.9
7	6.7	35	35.5	HCl; aq. 32 %	1.86	75.9	3610	96.6
8	3.25	35	32.5	HCl; aq. 32 %	0.93	43.5	4262	96.6